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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

OCT 24 1983

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM:

SUBJECT:

50534-8. Chlorothalonil-Residue estimates in pro-

cessed foods.

FROM:

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Hazard Evaluation Division (TS-769)

THRU:

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TO:

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Registration Division (TS-767)

and

Toxicology Branch

Hazard Evaluation Division (TS-769)

Diamond Shamrock has requested that the estimates of the hazard resulting from consumption of chlorothalonil treated cucumbers, melons, pumpkins snap beans and tomatoes be based on the actual anticipated residues in these commodities at the point of consumption rather than the established tolerance levels. Tolerances for residues of chlorothalonil and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile have been established at 5 ppm on cucumbers, melons, pumpkins, snap beans and tomatoes (40CFR180. 275).

The metabolism of chlorothalonil in plants and animals has been reviewed in detail in conjunction with PP#s 7F0599, 1F1024, 2F1230, 4F1502, 6F1799 and 6G1871.

The residue in plants (corn and tomatoes PP #7F0599 and potatoes PP #9F0743) is mainly surface in nature. Foliar deposits of chlorothalonil do not translocate and there is no uptake from roots to aerial plant parts. The parent compound and the 4-hydroxy metabolite are the residue of concern.

The residue data submitted in support of this request will be discussed below under individual commodities.

Melons and Pumpkins

Federally registered uses permit multiple applications at rates of up to 2.25 lbs act/A.

A summary of residue data submitted previously with PP's # 1F1024 and 7F0599 accompanies this request. Following 5-11 applications at rates of up to 2.25 lbs act/A residues of chlorothalonil per se in or on whole cantaloupes, muskmelons, honeydew melons, winter squash, watermelons and pumpkins ranged up to 2.26 ppm at PHI's of 0-7 days. The highest residue value reflects 7 applications of 1.5 lbs act/A and a 7 day PHI. Residues of 4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) in whole cantaloupes which received 7 applications of 3 lbs act/A were <0.08 ppm at a 4 day PHI.

Residues of chlorothalonil generally concentrated in the rind ranging up to 9.36 ppm in or on cantaloupe rind on the day of the last of 7 applications of 2.25 lbs act/A. Residues of DS-3701 are reported as 0.00 ppm in or on watermelon rind at 14 days following 7 applications of 1.12 lbs act/A. Residues of chlorothalonil and DS-3701 were 0.05-0.10 ppm and 0.14 ppm, respectively in the edible portion of cantaloupes at 0-4 days following 5-7 applications of 2.25 lbs act/A.

Based on the available data we estimate that residues of chloro-thalonil and DS-3701 will not exceed 0.2 ppm in or on the edible portion of melons and pumpkins as a result of the registered uses of chlorothalonil.

Cucumbers

Federally registered uses permit multiple applications at rates of up to 2.25 lbs act/A.

A summary of residue data submitted previously in support of PP #1F1024 accompanies this request. Following up to 13 applications at rates of up to 2.25 lbs act/A residues of chlorothalonil per se in or on whole unwashed cucumbers ranged up to 2.90 ppm at PHI's of 0-7 days Residues of DS 3701 were < 0.03 ppm at a 0 day PHI.

The differences between residue levels found in midget pickles and slicing size varieties are not considered significant enough to warrant differentiation in the residue estimates on the basis of variety or size.

When cucumbers were analyzed following a water wash residues of chlorothalonil decreased from 0.26-0.45 ppm and 0.08-0.10 ppm to 0.02-0.03 ppm and 0.01 ppm, respectively Residues of chlorothalonil in peeled cucumbers were 0.01 ppm while residues in the peelings were 1.26 ppm following 5 applications of 1.12 lb act/A.

Based on the limited processing daa submitted with this request we estimate that residues of chlorothalonil and DS-3701 in washed cucumbers and in peeled cucumbers will not exceed 1 ppm as a result of registered uses of chlorothalonil. We note that the pickling process involves a water wash.

Snap Beans

Federally registered uses permit multiple applications at the rate of up to 2.25 lbs act/A with a 7 day PHI. There is a restriction against grazing in treated areas or feeding treated plant parts to livestock.

The registrant asserts that processing of snap beans will significantly reduce residues of chlorothalonil on treated beans.

In the study, "Distribution of 2,4,5,6-tetrachloroisophthalonitrile and 4-hydroxy-2,5,6-trichloroisophthalonitrile among the products of snapbean processing" submitted with this request treated snapbeans were processed for canning or freezing. Residues of chlorothalonil and its metabolite DS-3701 were measured by a method similar to method I of PAM II. Validation data have been submitted. Recoveries from bean waste and plants fortified with 0.10 ppm chlorothalonil and DS-3701 averaged 81-89% and 75-80% respectively.

Treated snapbeans intended for canning contained up to 0.88 ppm chlorothalonil upon arrival to the factory. Air cleaning removed trash harvested with the snapbeans and reduced snapbean residues to 0.54 ppm chlorothalonil. After the washing step no chlorothalonil or DS-3701 (<0.01 ppm) was detected in the processed snapbeans. Most of the residue was found in the trash which contained up to 7.20 ppm chlorothalonil.

Similarly, treated snapbeans destined for freezing contained up to 0.80 ppm chlorothalonil upon arrival at the factory. Each step in the processing (washing, slicing, blanching) reduced the residue levels until ND (<0.01 ppm) residues of chlorothalonil or DS-3701 were found in snapbeans which had undergone steam or water blanching.

Based on these data we estimate that residues of chlorothalonil and its metabolite DS-3701 are not expected to exceed 0.1 ppm in or on commercially processed; canned or frozen snapbeans.

Tomatoes

Federally registered uses permit multiple applications at the rate of up to 2.25 lbs act/A.

Two studies have been submitted in support of the assertion that residues of chlorothalonil and DS-370l are reduced in treated tomatoes upon processing. "The Fate of Chlorothalonil Residues in the Processing of Tomatoes" and "The Effect of Commercial Processing Upon the Residues of Chlorothalonil on Tomatoes."

In the first study, field grown tomatoes received 7-9 applications at the rate of 1.5-2.25 lbs act/A. Unwashed whole tomatoes contained from 1.61-3.25 ppm chlorothalonil and no residues of DS-3701. After a mildly caustic wash simulating commercial processing residues of chlorothalonil ranged from 0.01-0.17 ppm. Residues of chlorothalonil in the dry pomace (peel, seeds, core) ranged from 0.025 ppm -0.04 ppm while residues of chlorothalonil were <0.01 ppm in Traces <0.02 ppm of DS-3701 were detected in the pomace the juice. In the second part of this study field grown tomatoes and juice. received 5 applications at the rate of 2.25 lbs act/A. whole tomatoes contained from 3.56-4.36 ppm chlorothalonil and no residues of DS-3701. The processing did not involve a caustic wash. Residues of chlorothalonil and DS-3701 ranged from 0.55-0.70 ppm and 0.10-0.14 ppm, respectively, in dry cannery waste (pomace) and were <0.01 ppm in canned tomatoes, tomato paste and tomato juice.

In the second study field grown tomatoes received 7 applications at the rate of 2.12-4.25 lbs act/A. Samples were harvested on the day of the last application and were commercially processed.

Residues of chlorothalonil and DS-3701 were determined by a method similar to Method I of PAM II. Reported recoveries from tomatoes, juice, pomace and paste fortified with 0.01 ppm-5.22 ppm chlorothalonil and 0.01-0.55 ppm DS-3701 ranged from 46-100% and 42-125% (excluding juice) respectively.

Residues of chlorothalonil in or on unwashed tomatoes ranged from 1.44-2.97 ppm and 4.36-5.08 ppm, respectively, for the two application rates. Residues of DS-3701 were \leq 0.02 ppm. Residues of chlorothalonil in or on washed tomatoes ranged from 0.50 ppm-0.88 ppm and 1.11-1.29 ppm, respectively. No detectable residues of DS-3701 (<0.01 ppm) were found.

The table below summarizes the results of the study.

MAXIMUM RESIDUES (PPM) OF CHLOROTHALONIL (DS-2787)
AND DS-3701 ON TOMATOES AND PRODUCTS
RESULTING FROM THE COMMERCIAL PROCESSING OF TOMATOES

		4.25 pts/A DS-2787 DS-3701 ppm ppm		8.50 pts/A		
Sample				DS-2787 DS-3701 ppm ppm		
Unwashed	•	2.97	0.02	5.08	0.01	
Washed		0.88	ND	1.29	ND	
Pomace	(Unspecified whether wet or dry)	2.48	0.02	3.85 0.79	0.04	
Paste		ND	0.01	0.03	0.03	

 $[\]frac{1}{2}$ ND = <0.01 ppm DS-3701 for whole tomatoes and pomace

 2 ND = <0.005 ppm DS-2787 for juice

There is a caveat that the above data may not be applicable to those processes in which tomato skins are not separated from the whole fruit until later stages of processing.

Based on the available data we conclude that residues in washed tomatoes and processed tomato products (human foods) are not likely to exceed 1 ppm as a result of the registered uses of chlorothalonil.

 $^{^{3}}$ ND = <0.01 ppm DS-2787 and <0.01 DS-3701 for paste.

The Effects of Cooking Upon Chlorothalonil Residues

The registrant has submitted two reports to demonstrate the effect of cooking on the residues of 2,4,5,6-tetrachloroisophthalonitrile. ¹⁴C-phenyl labeled chlorothalonil was cooked under various cooking conditions with water, chopped green beans and tomatoes.

Under reflux conditions chlorothalonil was hydrolyzed as identified by TLC and autoradiography to DS-3701 (24.4%) and 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221). No loss or degradation of chlorothalonil was observed when the cooking was done in a pressure cooker. Under distillation conditions only the parent compound was identified in the distillate. When 14C-DS-3701 was cooked alone no hydrolysis was observed.

More than 84% of chlorothalonil was lost through volatilization from open or loosely sealed vessels.

Thus we conclude that snapbeans and tomatoes cooked in an uncovered or loosely covered container may contain up to 1 ppm of chlorothalonil and its metabolites DS-3701 and DS-19221 depending upon the extent of washing prior to cooking.

Cooking in a pressure cooker would not significantly reduce residues on the treated vegetables.

Conclusions

- 1. Tolerances for residues of chlorothalonil and its metbaolite 4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701) have been established at 5 ppm on cucumbers, melons, pumpkins, snapbeans and tomatoes.
- 2. The residue in plants is mainly surface in nature. Foliar deposits of chlorothalonil do not translocate and there is no uptake from roots to aerial plant parts. The parent compound and the 4-hydroxy metabolite are the residues of concern.
- 3. Residues of chlorothalonil and DS-3701 will not exceed 0.2 ppm in or on the edible portion of melons and pumpkins as a result of the registered uses of chlorothalonil.
- 4. Residues of chlorothalonil and DS-3701 in washed cucumbers and in peeled cucumbers will not exceed 1 ppm as a result of the registered uses of chlorothalonil.

- 5. Residues of chlorothalonil and its metabolite DS-3701 are not expected to exceed 0.1 ppm in or on commercially processed canned or frozen snapbeans.
- 6. Residues in washed tomatoes and processed tomato products (human foods) are not likely to exceed 1 ppm as a result of the registered uses of chlorothalonil.
- 7. Residues of chlorothalonil and its metabolites 4-hydroxy-2,5,6-trichloroisophthalonitrile and 3-cyano-2,4,5,6-tetrachlorobenzamide are not expected to exceed 1 ppm in snapbeans and tomatoes cooked in uncovered or loosely covered containers.

Cooking in a pressure cooker would not significantly reduce the levels of residues in the treated vegetables.

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cc: Chlorothalonil S.F., R.F., Circu., E.Zager, Commodity
Definition S.F.,
RDI: R. Hummel, 10/24/83; R. Schmitt, 10/24/83